Electroreduction of Palladium(II) from Glycinate Electrolyte

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Complexone - based electrolytes are widely used in electroplating for depositing functional coatings of metals and alloys. This is due to the fact that complexones are nontoxic compounds, are easy to reclaim, readily available, indifferent to electrochemical processes.

The state of palladium(II) ions in a glycinate electrolyte has been studied to develop a promising palladium plating electrolyte for depositing functional coatings, which are suitable for use as palladium catalysts in inorganic and organic synthesis. The ionic composition of the electrolyte under investigation in bulk solution, in the cathode layer and on the electrode surface has been calculated. The dependence of concentration changes within the diffusion layer on polarizing current magnitude, the ratio of the main constituents and solution pH has been established. It has been shown that the main forms of existence of palladium ions in the cathode layer of glycinate electrolyte are $Pd(Gl)_2$ complexes, and that those of ligand are Gl^- and HGl. The values of concentration polarization in the cathode layer have been calculated and compared with experimental data. In has been found that the reduction of palladium(II) from glycinate electrolyte is described by mixed-kinetics relationships. The electrode process rate along with transfer reaction sluggishness is controlled by the diffusion of ions being reduced to the electrode surface. When the equilibrium concentration of ligand is increased, the contribution of transition overpotential to the overall electrode polarization decreases and becomes practically negligible at a certain Pd(II)-glycine concentration ratio, i e the overpotential observed in this case is pure diffusion one in its nature.

The kinetic parameters and orders of electrode reaction for ligand and hydrogen ions, the activation energy of diffusion and activation energy of palladium(II) discharge from glycinate electrolyte containing a small excess of ligand have been determined over a wide pH range by voltammetric and chronopotentiometric measurements on a palladium electrode. The transfer reaction activation energy value has been estimated. The total activation energy value of the electrode process is proportional to the overall overpotential of the corresponding electrochemical reaction. A method for the determination of diffusion activation energy from nonstationary polarization curves is proposed.

The composition of electrochemically active ions directly involved in the transfer reaction has been determined. The equilibrium constant of electroactive complex formation reaction has been determined. A mechanism of palladium(II) reduction from glycinate electrolyte is proposed.